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Final Report

Thomas J. Meyer

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Charge Transfer In Multiple Chemical systems

Based on the support of AROD, we have investigated charge transfer processes in chemical systems containing more than one redox site. These systems include ligand-bridged metal dimers and polymeric materials that have redox sites that are incorporated either by ion exchange or by direct chemical linkage.

A. Mixed-Valence Dimers

In mixed-valence dimers the position and extent of the delocalization of the odd electron depends on the metals and on the bridging and nonbridging ligands.⁽¹⁾ We have prepared mixed metal dimers $[(bpy)_2(Cl)Os^{II}(pz)Ru^{II}(NH_3)_5]^{3+}$ ($bpy=2,2'$ -bipyridine; $pz=pyrazine$) in which the metal-ligand combination at the two sites lead to redox potentials for the $Os(III)/(II)$ and $Ru(III)/(II)$ couples which are nearly of the same magnitude. Because of the difference in the sensitivity of the potentials of the two couples to solvent, in the mixed-valence forms, intramolecular electron transfer can be incuded by changes in the solvent. We also found that variations in solvent appear to affect the extent of delocalization of the odd electron.⁽²⁾

Oxidation of transition-metal complexes cotaining aqua ligands leads to an enhanced acidity and to redox couples whose potentials are pH-dependent. we found that in the ligand-bridged, mixed-valence dimer $[(trpy)-(bpy)Os^{III}(4,4'-bpy)Ru^{II}(H_2O)(bpy)_2]^{5+}$ ($trpy=2,2',2''$ -terpyridine), which contains both an aqua-based, pH-dependent couple and a pH-independent couple, changes in pH can be utilized to induce intramolecular electron transfer across the ligand-bridge. In the twice-oxidized $Os(III)$ - $Ru(III)$ dimer, pH induced intramolemlar electron transfer can be used to concentrate the stored redox equivalents at a single site, thus gaining a significantly enhanced oxidative reactivity toward an organic substrate.⁽³⁾

From the solvent dependence of the absorption band energies for metal to metal charge transfer bands in several symmetrical ligand-bridged mixed-valence dimers, water emerges as an anomalous solvent. Explanations based on specific ligand - solvent interactions or the

involvement of high frequency hydroxyl stretching modes were shown to be inconsistent with the available results.

The experimental observations can be accommodated by postulating the involvement of relatively high-frequency librational modes known to exist in water. The observation of anomalously high MMCT band energies in water has significant implications for related electron transfer reactions such as thermally activated self-exchange.⁽⁴⁾

In the study of mixed-valence compounds, ligand-bridged dimers based on the $[(\text{NH}_3)_5\text{Ru}^{\text{III/II}}]$ couple have played a central role. Notable examples include the Creutz and Taube ion, $[(\text{NH}_3)_5\text{Ru}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{5+}$ (pz=pyrazine), where the question of localization vs. delocalization is a source of continuing debate, and the analogous 4,4'-bipyridine-bridged dimer, $[(\text{NH}_3)_5\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{5+}$, where the valences appear to be trapped and the properties are well-defined in terms of available theory. We have reinvestigated a particular property of the latter ion, the solvent dependence of the energy of its intervalence transfer (IT) or metal to metal charge transfer (MMCT) absorption band. On the basis of the results of our study and in light of recent development in the area, we conclude that (1) there is a considerable contribution to the apparent IT band energy arising from the existence of multiple IT transitions, (2) application of dielectric continuum theory to the solvent dependence of the IT band energy is not quantitatively successful, and (3) solvent effects whose origins arise at the molecular level may play a role in dictating the observed absorption band energies.⁽⁵⁾

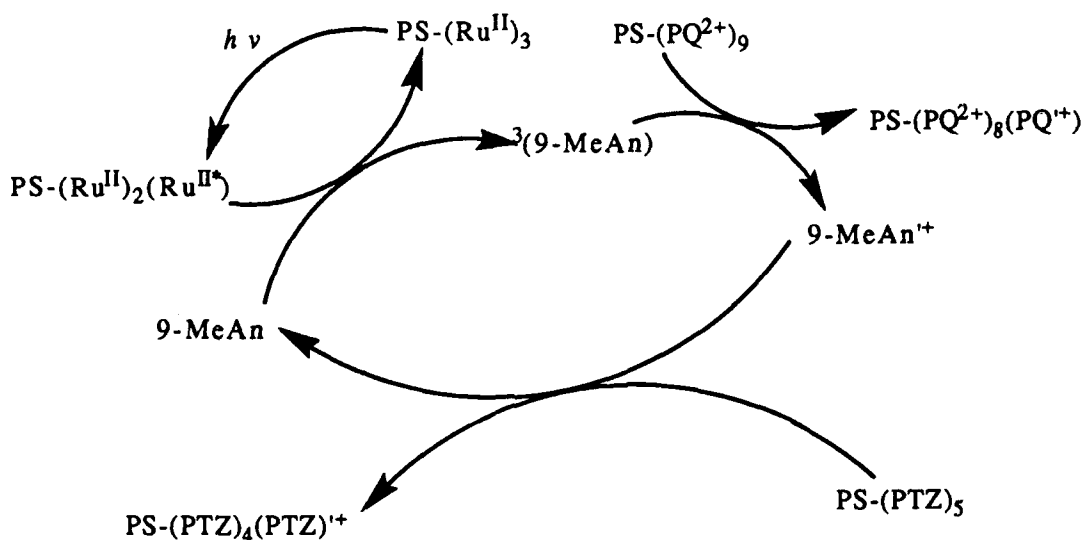
B. Soluble Polymers

We have investigated control of intramolecular redox events following optical excitation is based on the chemical modification of soluble polymers. The particular polymer which has provided the basis for most of our work is a 1:1 copolymer of polystyrene and chloromethylated polystyrene. We have exploited the chloride displacement chemistry for chemical attachment via the formation of amines from amides, ethers from alkoxides, and esters from carboxylates. The displacement chemistry has allowed us to bind electron transfer donors like -PTZ, electron transfer acceptors like $-\text{MQ}^+$, and Ru-bpy based chromophores using either ester or other links. The resulting polymers have been characterized by NMR and

elemental analysis. The extent of loading of the polymers by either quenchers or chromophores can be adjusted by controlling the reaction conditions. In addition there is sufficient synthetic flexibility that it is possible to coinorporate various combinations of chromophores and quenchers. In fact, the background synthetic chemistry in this area is well advanced and gives us the opportunity of preparing a series of interesting mixed function polymers where chemical content can be controlled on demand.

Results are available from two quenching studies on the polymer based systems. The first was a take - off on an earlier experiment in which optical excitation of $[\text{Ru}(\text{bpy})_3]^{2+*}$ in acetonitrile solution containing both PQ^{2+} and DMA (DMA is Me_2NPh) was shown to lead to the separated redox products PQ^+ and DMA^+ . We investigated the transferral of this reaction into soluble polymers. In particular, experiments were carried out in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ in which both the $-\text{PQ}^{2+}$ oxidant and $-\text{PTZ}$ reductant were bound to separate strands of chemically derivatized polystyrene polymers. Following excitation of the metal complex in solutions containing the polymer-bound quenchers, a series of electron transfer events occur but now with the electron transfer donor and acceptor on separate polymeric strands. Because of relative slow diffusion of the photoproducted oxidative and reductive equivalents in $\text{PS}-(\text{PQ}^{2+})_7(\text{PQ}^+)$ and $\text{PS}-(\text{PTZ})_{10}(\text{PTZ}^+)$, there is an extensive prolongation (10^2 to 10^3) of the time during which the oxidative and reductive equivalents are stored before back electron transfer can occur⁽⁶⁾. In a second experiment the same electron transfer donor and acceptor and Ru-bpy based chromophore bound to the polymeric backbone by either links were all present in solution on separate polymeric strands. Under conditions relatively dilute in polymer-bound chromophore and added quenchers, photolysis of the solution leads to no quenching because of relatively slow diffusion of separated polymeric strands. However, a somewhat convoluted electron and energy shuttling mechanism can be set up by adding an anthracene derivative to the solution.⁽⁷⁾ Appropriate derivatives of anthracene are known to quench $[\text{Ru}(\text{bpy})_3]^{2+*}$ with efficiencies of ~ 1 , if energy transfer is spontaneous, and the resulting anthracene triplet undergoes subsequent facile oxidative quenching by

PQ^{2+} . When 9-methyl anthracene (9-MeAn) is added to a solution containing the chromophore and oxidative and reductive quenchers on separate polymeric strands in acidified DMF solutions, the sequence of reactions shown in scheme I occur as shown by laser photolysis. In the series of steps (shown in scheme I) a sequence of energy and electron transfer shuttling steps is utilized to achieve the same end as in the previous experiments where the photoinduced oxidative equivalents were transiently stored on separated polymeric strands.



Scheme I

C. The Immobilization of Catalysts of Polymeric Films and Polymer Supports

Chemically modified electrodes containing the ruthenium and osmium oxo-bridged dimers $[(bpy)_2(H_2O)M^{III}]_2O^{4+}$ have been prepared by cation exchange into films of partially hydrolyzed p-chlorosulfonated polystyrene deposited onto glassy carbon electrodes. Both similarities and differences appear in comparing solution and film redox and acid-base properties: (1) As in solution the dimers undergo an initial one-electron oxidation, but the charge-transfer processes leading to higher oxidation states are inhibited in the polymeric film. (2) Reduction

of the dimer leads to cleavage and formation of the monomer $(bpy)_2M(H_2O)_2^{2+}$ in the film. (3) In the film environment the dimers are less acidic than in solution. The catalytic oxidation of chloride ion by electrodes containing the Ru dimer has been studied in detail. Oxidation of 0.1M LiCl solution occurs with an initial current density of 100 mA/cm², and 26000 turnovers/Ru site are obtained before deactivation of the catalyst occurs. Rotated disk experiments show that the oxidation of Cl⁻ is independent of rotation rate but linearly dependent on [Cl⁻]. Deactivation of catalyst appears to occur by oxidatively induced anation, possibly involving binding of sulfonate sites on the polymer to the dimer^[8].

D. Controlling Redox Effects in Polymeric Films

We found that when oxidized, transition-metal aqua complexes characteristically become more acidic and, consequently, their redox couples become pH dependent. A bilayer of thin polymeric films on a glassy carbon electrode was prepared by electropolymerizing $[(bpy)_2Os(vpy)_2][PF_6]$ (vpy=4-vinylpyridine) to the inner layer, and adding as an outer layer Nafion[®] into which the complex $[(bpy)_2(py)Ru(OH_2)]^{2+}$ was ion exchanged. The Os(III)/(II) couple is pH independent with $E_{1/2}=0.55V$ while $E_{1/2}$ for Ru(III)/(II) couple varies from 0.76 to 0.20V over the pH range 1 to 10, $(bpy)_2(py)Ru^{III}-OH_2^{2+} + e^- + H^+ \rightarrow (bpy)_2(py)Ru^{II}-OH_2^{2+}$.

At pH 5.0 the potentials of the couples in the inner and outer films are the same. By decreasing the pH in the external solution to pH = 2.0 with the electrode potential held at 0.60V (i.e., both films initially as M(III)), a long - range electron transfer occurs from the electrode through the intervening Os film to Ru(III) sites in the outer film. Upon returning the pH in the external solution to 5.0, the reverse process occurs, and long-range electron transfer from Ru(II) to the electrode is mediated by the inner film⁽⁹⁾.

Electrochemical and spectroelectrochemical experiments on the complexes $[(bpy)_2(py)Ru^{II}-OH_2]^{2+}$ and $[(trpy)(bpy)Ru^{II}(OH_2)]^{2+}$ (trpy= 2,2',6,2"- terpyridine) with Nafion[®] films coated on electrodes demonstrate

that the complexes partition amongst three chemically distinct regions or phases. As Ru(II) the complexes reside both in an electroactive phase and, based on the pH dependence of the Ru(III)/(II) couples, e.g., $[(bpy)_2(py)Ru^{III}(OH)]^{2+} / [(bpy)_2(py)Ru^{II}(OH_2)]^{2+}$, in two electroactive phases. Partitioning amongst the three phase depends upon the pH of the external solution and on the oxidation state and proton content of the complex. Addition of alcohols releases the complex from the electroinactive phase but at the expense of loss of the bound water molecule and binding to the sulfonate sites by anation and, therefore, to a fourth distinct chemical or physical state in which the complex can exist within the Nafion[®] films.⁽¹⁰⁾

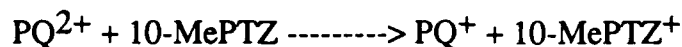
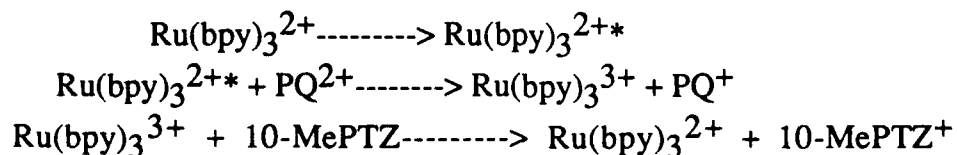
E. Synthesis and Coordination Chemistry of Polymeric Films on Electrode Surfaces

Reductive electrochemical polymerization of vinyl-containing transition metal complexes has provided a convenient preparative route to redox active, thin polymeric films on metallic and semiconductor electrodes. A significant advance in the underlying preparative chemistry of chemically modified electrodes was made based on octahedral $Zn(vbpy)_3^{2+}$ and the square-planar complexes $[M(vbpy)(COD)]^+$ ($vbpy=4$ - Vinyl-4'-methyl- 2',2'-bipyridine; COD=1,5-cyclooctadiene; $M=Rh(I)$ or $Ir(I)$). In both cases the metal ions are relatively labile and can be removed to give metal ion free films that have different coordination chemistries. Alternatively, the metal ions can be replaced by using suitable metal precursors to give redox-active films containing different metal ions. Our approach differed from those of previous studies in that it emphasized preparative chemistry at the polymer electrode interface.⁽¹¹⁾

Several dozen Fe, Ru, Os, Re and Co complexes containing the ligands 4,4'-distyryl-2,2'-bipyridine(DSB) and 4,4'-dis(p-methylstyryl)-2,2'-bipyridine (MeDSB) have been prepared . The ligands undergo coupling reactions when the complexes are reduced electrochemically, resulting in the formation of smooth and adherent electroactive polymeric films on Pt electrodes. Evaluation of the relative rates of electropolymerization for selected metal complex monomers shows that the DSB and MeDSB ligands lead to slower electropolymerizations than do the related ligands $vbpy(4$ -

vinyl-4'-methyl-2,2'-bipyridine) and vpy(4-vinylpyridine) in analogous complexes. The stability of the DSB and MeDSB ligands was helpful in the synthesis of novel electropolymerizable monomers such as $[\text{Os}(\text{DSB})_3]^{2+}$, $[\text{Os}(\text{MeDSB})_3]^{2+}$, $[(\text{DSB})_2\text{M}(\text{CO})\text{Cl}]^+$ ($\text{M}=\text{Ru}, \text{Os}$), and $[(\text{DSB})\text{Re}(\text{CO})_3\text{X}]$. The last complex is a CO_2 reduction catalyst. Correlations between monomer composition and polymer characteristics were revealing, showing, for example, that poly- $[(\text{MeDSB})_3\text{M}]^{2+}$ films exhibit faster electron transport and are more permeable than previously studied poly- $[\text{Ru}(\text{vbpy})_3]^{2+}$ films.⁽¹²⁾

The preparation of thin polymeric films containing redox couples on carbon or platinum electrodes was described based on the oxidative electropolymerization of substituted pyrroles. The redox couples involved are pyrrole derivatives of the chromophore $[\text{Ru}(\text{bpy})_3]^{2+}$, the electron transfer acceptor paraquat (PQ^{2+}) and electron transfer donor phenothiazine. Copolymeric films containing more than one redox couple were prepared having film structures in which there are spatially segregated bi- and trilayers, each layer containing a different couple. We describe the results of a series of studies designed to utilize the film based pyrrole chemistry to assemble a variety of derivatized polypyrrole film structures. The redox active groups were the electron transfer donor 10-propylphenothiazine (PTZ), the electron transfer acceptor 1,1'-dipropyl-dinium (PQ^{2+}) and the metal to ligand charge transfer (MLCT) chromophore $[\text{Ru}(\text{pyr-bpy})_3]^{2+}$ ($\text{pyr-bpy}=4-(2\text{-pyrrol-1-ylethyl-4'-methyl-2,2'-bipyridine})$). The combination chosen was of interest to us on photochemical grounds. In fluid solutions containing analogues of the three components in appropriate concentrations, excitation of the chromophore was followed by oxidative quenching and capture of $[\text{Ru}(\text{bpy})_3]^{3+}$ by 10-methylphenothiazine (10-MePTZ),



which results in the net photoreduction of separated oxidative and

reductive equivalents based on 10-MePTZ⁺ and PQ⁺. We hoped to transfer the photochemistry to the polymeric film environment in such a way that the photoproduced oxidative and reductive equivalents were directed toward spatially separated regions of the film and so to begin to mimic the characteristics of the p/n junction in solid state devices.⁽¹³⁾

F. Characterization of Metal Complex Containing Polymeric Films

There is a continuing need for spectroanalytical techniques for the identification, characterization, and analysis of thin polymeric films on electrodes. In many cases a metallic substrate is required for the fabrication of the polymeric film. One example is electropolymerization, where the polymer is formed at the electrode surface. Another is the chemical modification of prefabricated polymers during which the integrity of the film could not be maintained without specific adsorption onto a solid support such as platinum. We used a procedure for obtaining both transmission IR and visible spectra of the same electropolymerized or spun-cast polymeric film on platinized sodium chloride plates. If the metallic layer is sufficiently thin, the salt plates remain semitransparent in both the IR and visible regions and yet are sufficiently conductive to use as electrodes.⁽¹⁴⁾

Another way to characterize polymeric film is to use Secondary Ion Mass Spectroscopy (SIMS). The polymeric matrix was chlorosulfonated polystyrene (~1000 Å thick) cast onto a smooth platinum substrate, and following subsequent incorporation of metal complexes containing Ru, Re, or Zn by chemical binding, the SIMS technique was found to be chemically selective and sensitive to the Ru, Re, and Zn sites in the polymeric films. Qualitative assays of the film using secondary ion mass spectra were relatively easy, but determinations of the spatial distribution of metal sites throughout the films required highly controlled sample preparation. The results of a series of studies on polymeric films containing various levels of the Ru complex showed that signals for Ru⁺ are influenced by local variations in ion yield, i.e., ion yield transitions near the polymeric surface and at the polymer/platinum interface. A normalization procedure based on comparisons of Ru⁺ to O⁺ secondary ion intensities reduces the influence of such artifacts in the analysis of the concentration depth profiles of the complexes within the polymeric films.⁽¹⁵⁾

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Participating Scientific Personnel

Vining	Ph. D. Awarded
Surridge	Ph. D. Awarded
Margerum	Ph. D. Awarded
Neyhart	Research assistant
McClanahan	Research assistant
Downard	Research assistant
Loeb	Research assistant
Olmsted,III	Research assistant